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Paper-ID 58436
Paper title A techno-economical analysis of biobutanol production integrated with pervaporation
Presentation format Oral presentation
Date of submission 30.01.2017 19:52 Uhr
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Content

The production of n-butanol with clostridial strains has a colourful history and recently surpassed its 100th anniversary. The solvent concentration at the end of a fermentation barely exceeds 2 wt%, leading to high distillation costs, high waste water volumes and low productivities due to product inhibition. Therefore, the production of n-butanol and acetone were replaced with a cost-effective petrochemical alternative. However, depletion of oil supplies is a fact, bringing the interest in biobutanol production from (lignocellulosic) biomass back into the limelight. The quest for increased solvent productivities, decreased process flows & especially decreased energy consumption explain the interest in in situ product recovery (ISPR) technologies for n-butanol production from biomass. As a consequence, a plethora of research results are available on a multitude of ISPR technologies.

Nevertheless, introduction of these technologies for fermentative n-butanol production on an industrial scale has not materialized yet due to the risks associated with introducing novel technology on large scale, and the required in-depth knowledge to size and design an integrated production plant.

A base-case and process alternative for fermentative n-butanol production at a capacity of 100 ktonnes per year is presented in this study. To evaluate the economic potential of pervaporation coupled to fermentation, rational butanol production costs for the two cases were calculated. The base-case consists of a multi-stage acetone-butanol-ethanol fermentation with default downstream processing, i.e. beer stripping and hetero-azeotropic distillation. The alternative is a continuous hybrid process where default downstream processing is complemented with organophilic pervaporation for recovery of solvents during the fermentation.

Paper-ID 52491

Paper title BIO-GO: Conversion of Bio Gas and Pyrolysis Oil to Synthetic Fuels through reforming, methanol synthesis and MTG processes operated in a miniplant in an modular containerised environment

Presentation format Oral presentation

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Content

BIO-GO-For-Production is a Large Scale Collaborative Research Project co-ordinated by the author, which was started late 2013 in the scope of the 7th Framework Program of the European Commission. It aims to achieve a step change in the application of nanocatalysis to sustainable energy production through an integrated, coherent and holistic approach utilizing novel heterogeneous nanoparticulate catalysts in fuel syntheses.

BIO-GO researches and develops advanced nanocatalysts, which are allied with advanced reactor concepts to realise modular, highly efficient, integrated processes for the production of fuels from renewable bio-oils and biogas. Principal objectives are to develop new designs, preparation routes and methods of coating nanocatalysts on innovative micro-structured reactor designs, enabling compact, integrated catalytic reactor systems that exploit fully the special properties of nanocatalysts to improve process efficiency through intensification.

An important aim is to reduce the dependence on precious metals and rare earths. Catalyst development is underpinned by modelling, kinetic and in-situ studies, and is validated by extended laboratory runs of biogas and bio-oil reforming, methanol synthesis and gasoline production via the MTG process to benchmark performance against current commercial catalysts. The 4-year project culminates in two verification steps: (a) a 6 month continuous pilot scale catalyst production run to demonstrate scaled up manufacturing potential for fast industrialisation (b) the integration at miniplant scale of the complete integrated process to gasoline production starting from bio-oil and bio-gas feedstocks.

The focus of the presentation will be on the first results from the operation of the miniplant with emphasis on the pyrolysis oil reforming and synthesis gas purification steps downstream.

Acknowledgement: The work presented in the current abstract is supported by the European Commission in the scope of the 7th Framework Programme in the Integrated Project BIOGO (www.biogo.eu)

Paper-ID 27391
Paper title Biodiesel production using in-situ transesterification of spent coffee grounds
Presentation format Poster
Date of submission 25.01.2017 06:55 Uhr
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Content

Abstract

Based on the International Coffee Organization, 5,817,500 ton of coffee waste is generated every year. Most of spent coffee grounds (SCGs) are disposed by landfill, causing the problem to environment or ecosystem. Without energy intensive drying process, direct utilization of wet SCGs was investigated using in-situ transesterification with methanol that integrates extraction and conversion in a single process. For the reaction, excess methanol is required not only to break the linkages between glycerin and fatty acid, but also to inhibit the reverse-transesterification[1]. Higher acid concentration yields more fatty acid methyl ester (FAME) since the protonation of the carbon is the initial stage for the reaction [2]. Especially, oxidative acid catalyst such as nitric acid can not only decompose the brown color pigment (melanoidin) which is the impurity in biodiesel but also cause cleavage of long-chained FAMEs to short ones, which can not be used for a biodiesel. A water-immiscible and methanol-miscible organic solvent is needed for wet in-situ transesterification to prevent the water inhibition. It can draw out triglyceride (lipid) and methanol from the aqueous phase, therefore, it can facilitate mass transfer for the contact of the two reactants in the reaction[3]. The maximum yield was 16.75 wt.% when 8.33ml EtOH/g SCG and 1:1(v/v) chloroform as a co-solvent were used at 95°C under 2.82M H₂SO₄ catalyst. This study can suggest an eco-friendly way to recycle the municipal waste and utilize it as renewable energy.

References

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Paper-ID 30501
Paper title Biofuels reforming into syngas: design of structured catalysts and main process parameters
Presentation format Oral presentation
Date of submission 26.01.2017 15:41 Uhr
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Content

Design of efficient, inexpensive and stable to coking catalysts for transformation of natural gas/biogas/biofuels into syngas and hydrogen in the intermediate temperature range (600-800 °C) is a vital problem of sustainable and renewable energy field. This work presents results of extensive research aimed at design and characterization of such catalysts performance in transformation of a variety of biofuels (ethanol, acetone, ethyl acetate, anisole, glycerol, sunflower oil, turpentine oil). Nanocomposite active components were comprised of nanoparticles of metals/alloys (Ni, Co, Pt, Ni+Pt, Ni+Ru) supported on perovskites ($\text{La}_{1-x}\text{Pr}_x\text{Mn}_{1-y}\text{Cr}_y\text{O}_{3-d}$, CaTiO_3), fluorite Ln-Ce-Zr-O (Ln = La, Pr, Sm), rutile (Ln)TiO₂ and spinel $\text{Mn}_x\text{Cr}_{3-x}\text{O}_4$ oxides (both bulk samples and layers on Mg-doped alumina) with a high oxygen mobility and reactivity. Active components were loaded on structured substrates (Ni-Al foams; FeCrAl alloy foils/honeycombs, gauzes and microchannel platelets with protective corundum layers; microchannel FeAl(O) cermet) from suspensions with addition of surfactants, total loading up to 10-20 wt.%.

Activation of fuel molecules on Me/oxide sites and oxidants (H₂O, CO₂, O₂) on reduced sites of the oxide support along with fast oxygen diffusion to Me/support interface provide the efficient transformation of fuels into syngas preventing coking. Pulse and transient kinetic studies (including SSITKA) revealed that mechanism of ethanol reforming on these types of catalysts can be described by a simple red-ox scheme with C-C bond breaking as the rate determining stage. Strong metal-support interaction provides sintering stability of metal alloy nanoparticles.

In pilot tests of optimized structured catalysts packages/honeycombs in real feeds at short contact times, a high yield of syngas approaching equilibrium at ~700 °C was demonstrated in steam, dry, partial oxidation and mixed reforming of biofuels, main by-products being CH₄ (due to cracking) and C₂H₄ (due to dehydration). Suppression of surface acidity and O₂ addition to the feed decrease C₂H₄ content, thus preventing coking even for such fuels as glycerol, sunflower and turpentine oils. For radial-type reactor equipped with the internal heat exchanger partial oxidation or oxy-steam reforming of the mixture of natural gas and liquid biofuels allows to operate at inlet temperatures not exceeding 50-100 °C and producing up to 20 m³/h of syngas with the equilibrium composition of the exit stream. Stable performance was confirmed for more than 200 h time-on-stream. Mathematical modeling demonstrated absence of any heat transfer limitations due to a high thermal conductivity of substrates. No spallation or cracking of the active component layers supported on substrates was revealed.

Support by the FP7 Project BIOGO and Russian Ministry of Education and Science is gratefully acknowledged.

Paper-ID 56116

Paper title BIOMASS CATALYTIC FAST-PYROLYSIS OVER MgO AND ZnO SUPPORTED ON HIERARCHICAL ZEOLITES

Presentation format Oral presentation

Date of submission 30.01.2017 18:31 Uhr

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Content

Biomass Catalytic Fast-Pyrolysis over MgO and ZnO Supported on Hierarchical Zeolites

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Hierarchical zeolites, h-ZSM-5 and h-Beta, loaded with basic metal oxides, MgO and ZnO, were explored for the Catalytic Fast-Pyrolysis (CFP) of eucalyptus woodchips (EU). Characterization results revealed that loaded materials exhibit a high crystallinity degree. MgO or ZnO particles were not detected by means XRD or TEM analyses, indicating the formation of very small entities with a high and homogeneous dispersion over the zeolite surface. Likewise, the incorporation of metal oxides led to a significant reduction in the textural properties, due to a partial blockage of pores. Concerning the acidic properties, a decrease of the Brønsted acid sites occurred after metal oxide loading. At the same time, a new Lewis acidity with medium strength was generated, which resulted in an important increase of the overall acidity values, being higher in ZnO loaded materials than in the MgO supported ones (Table 1).

CFP experiments were performed in a lab scale fixed-bed reactor at 500 °C and atmospheric pressure using a nitrogen flow of 100 ml/min. In comparison with non-catalytic fast pyrolysis, the use of zeolitic catalysts increased coke and gas yields, leading to a detriment of bio-oil* (water free basis) production. Gas generation was higher over h-ZSM-5 materials, leading to a lower bio-oil* yield than h-Beta zeolites. However, attending to the bio-oil* quality, h-ZSM-5 catalysts showed a deeper deoxygenation degree. Likewise, MgO loaded samples provided enhanced energy yields, mainly due to higher bio-oil* production with lower oxygen content. Nevertheless, ZnO containing materials favored deoxygenation reactions via decarboxylation, which is the oxygen removal route with the lowest carbon loss.

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Table 1. Physicochemical properties of the assayed materials and catalytic performance.

Catalysts	Si/Al ^a	M.O. ^a (wt.%)	S _{BET} ^b (m ² /g)	V _{Total} ^c (cm ³ /g)	Acidity ^d (mmol/g)		Bio-oil* yield ^e (wt.%)	Oconc. ^e (wt.%)
					C _L	C _B		
Non-catalytic	-	-	-	-	-	-	42.2	39.0
h-ZSM-5	58.2	-	562	0.574	0.079	0.120	26.5	31.8
MgO/h-ZSM-5	-	8.4	398	0.506	0.306	0.032	28.4	28.4
ZnO/h-ZSM-5	-	9.7	434	0.508	0.378	0.022	25.4	29.1
h-Beta	24	-	779	0.507	0.177	0.142	31.8	39.1
MgO/h-Beta	-	8.7	400	0.310	0.483	0.042	34.6	37.0
ZnO/h-Beta	-	10.0	524	0.373	0.649	0.035	32.0	37.0

^a Measured with ICP/OES; ^b BET area per gram of catalyst; ^c Total pore volume at P/P₀ ≈ 0.98; ^d Pyridine adsorption/desorption at 150 °C followed by FTIR; ^e Catalytic pyrolysis of EU at 500 °C; *Water free basis

Paper-ID 35051

Paper title Catalytic properties of Zn- and Cr-containing magnetic oxide nanoparticles in the methanol synthesis from syngas

Presentation format Poster

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Content

We developed an ecologically sound synthetic pathway to novel Zn- and Cr-containing magnetic oxide nanoparticles (NPs) of different compositions using a one-pot procedure, where precursors are thermally decomposed in the reaction solution of prefabricated magnetite NPs stabilized by polyphenylquinoline, eliminating any intermediate purification procedures which might be otherwise required for a synthesis of multicomponent metal oxides NPs. All the samples consist of multicore and single-core NPs which are single crystals. A close contact between Zn^{2+} or Cr^{3+} and Fe_3O_4 species ensures exceptional catalytic properties of these catalysts in the reaction of syngas to methanol. The methanol accumulation rate for the Cr-containing magnetic oxide prepared with 0.5 mmol of the Cr precursor is much higher than that of Zn-containing magnetic oxides and approximately three orders of magnitude higher than the activity for the conventional $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst. Additional doping of this Cr-containing magnetic oxide with small amounts of Ni or La leads to even higher catalytic activity (by 40-49%). This exceptional catalytic activity of Cr-containing magnetic oxides as well as the stability of the catalyst after magnetic separation in five consecutive syngas-to-methanol reactions makes it a sustainable catalytic process, promising for industrial applications.

The research leading to these results has received funding from the European Community's Seventh Framework Programme [FP7/2007-2013] under grant agreement no. 604296.

Paper-ID 50196
Paper title Conversion of a bio-oil model compound on AlCl₃-modified porous catalysts investigated by in situ multi-nuclear solid-state NMR spectroscopy
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Content

The European Union (EU) focuses on a prevention of a dangerous climate change and set itself the 20-20-20 goal. Within this goal, the EU plans to reduce the greenhouse gas emission by 20 % (from 1990 levels), to increase the content of renewable energy resources by 20 %, and to improve the energy efficiency by 20 % until the year 2020 [1]. A main topic in the implementation of renewables is a blend of fossil-based and bio-oil-based feeds in the Fluid Catalytic Cracking (FCC) process. The co-feeding of bio-oil compounds, however, requires optimizing the performance of the FCC catalysts.

For the investigation of the catalyst framework and catalytically active sites, multi-nuclear solid-state NMR spectroscopy has shown a high potential. In the present work, this method was utilized for studying the effect of an alumination of porous catalysts, such as via a treatment with AlCl₃ vapor [2]. Aluminum atoms introduced by a treatment of siliceous materials with AlCl₃ coordinate at Si(2Si,2OH) and Si(3Si,1OH) sites, form tetrahedrally coordinated, pentacoordinated, and octahedrally coordinated aluminum species on the samples, and lead to the formation of Brønsted and Lewis acid sites [2]. Furthermore, in situ solid-state NMR spectroscopy was used for investigating the conversion of 2-ethylphenol (EP), chosen as bio-oil model compound, on AlCl₃-modified mesoporous SBA-15 and zeolites Y. The EP conversion was performed in sealed glass tubes at 723 K for 10 min. Strongly adsorbed and occluded reaction products, formed on the AlCl₃-modified porous catalysts, were investigated by ¹³C MAS NMR spectroscopy, while volatile reaction products were studied by ¹H spin-echo NMR spectroscopy of the sample volume inside the glass tubes on top of the catalyst layer.

We acknowledge the European Union Seventh Framework Program FP7-NMP-2013, under GA 604277 (FASTCARD), for financial support.

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Paper-ID 45006

Paper title The effect of the Zn:Cr ratio on the activity of ZnO/Cr₂O₃ catalysts applied in high-temperature methanol synthesis

Presentation format Poster

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Content

Recently, using biomass-derived syngas for the production of methanol has attracted considerable attention, since this process can be considered as utilizing renewable energy sources to generate alternative fuels. However, biomass-derived syngas, which normally contains high levels of sulfur and nitrogen, is still facing a number of challenges in the purification process. Unlike Cu-based catalyst, ZnO/Cr₂O₃ catalysts are very stable against sulfur and halogen impurities and may provide an alternative for the conversion of biomass-derived syngas to methanol without expensive purification. The present contribution describes the effect of the Zn:Cr ratio on the activity of ZnO/Cr₂O₃ catalysts prepared by co-precipitation in high-temperature methanol synthesis. In addition, the postulated model of the active phase in ZnO/Cr₂O₃ catalysts was examined by density functional theory (DFT) calculations.

Co-precipitation was performed at 65 °C and a constant pH of 7 using a 1 mol/L metal nitrate solution containing appropriate quantities of Cr(NO₃)₃ and Zn(NO₃)₂ as precursors and 1.2 M solution of Na₂CO₃ as precipitating agent. The resulting precipitate was aged under continuous stirring for 2 h, filtrated, washed repeatedly and dried at 120 °C for 18 h. Subsequently, the calcination was performed at 320 °C for 3 h in synthetic air. The calcined catalysts were applied in methanol synthesis from syngas at 60 bar and temperatures in the range from 260 to 300 °C. All computational calculations were carried out using DFT with the generalised gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional as implemented in the Vienna ab initio Simulation Package (VASP).

The test results show that the catalytic performance of the ZnO/Cr₂O₃ catalysts strongly depends on the Zn:Cr ratio. The highest methanol productivity was achieved with the Zn:Cr=65:35 catalyst. The optimal Zn:Cr ratio of 65:35 corresponds to the stoichiometric Zn:Cr ratio of the hydrotalcite-like precursor Zn₄Cr₂(OH)₁₂CO₃ obtained by co-precipitation. Combined with other characterization results, it is suggested that during calcination the hydrotalcite-like precursor decomposes forming the Zn-rich ZnCr₂O₄ spinel, which is considered to be the active phase of the catalyst in methanol synthesis. DFT calculations have further characterized this structure as an amorphous ZnO mono- or bilayer supported on the ZnCr₂O₄ spinel structure which contains undercoordinated Zn sites on the surface. Thus, this system is identified as the active methanol synthesis catalyst due to the lowest formation energy for oxygen vacancies, which are the active sites for CO hydrogenation.

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